

# ASSESSMENT OF PRODUCED WATER FOR AGRICULTURAL IRRIGATION OF EDIBLE CROPS: IDENTIFYING CHEMICALS OF INTEREST INTERIM PROGRESS REPORT JANUARY 24, 2019



*Robert Scofield and Bernard Beckerman*  
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# BACKGROUND

**GSI was retained by the Water Board to assist in 3 tasks:**

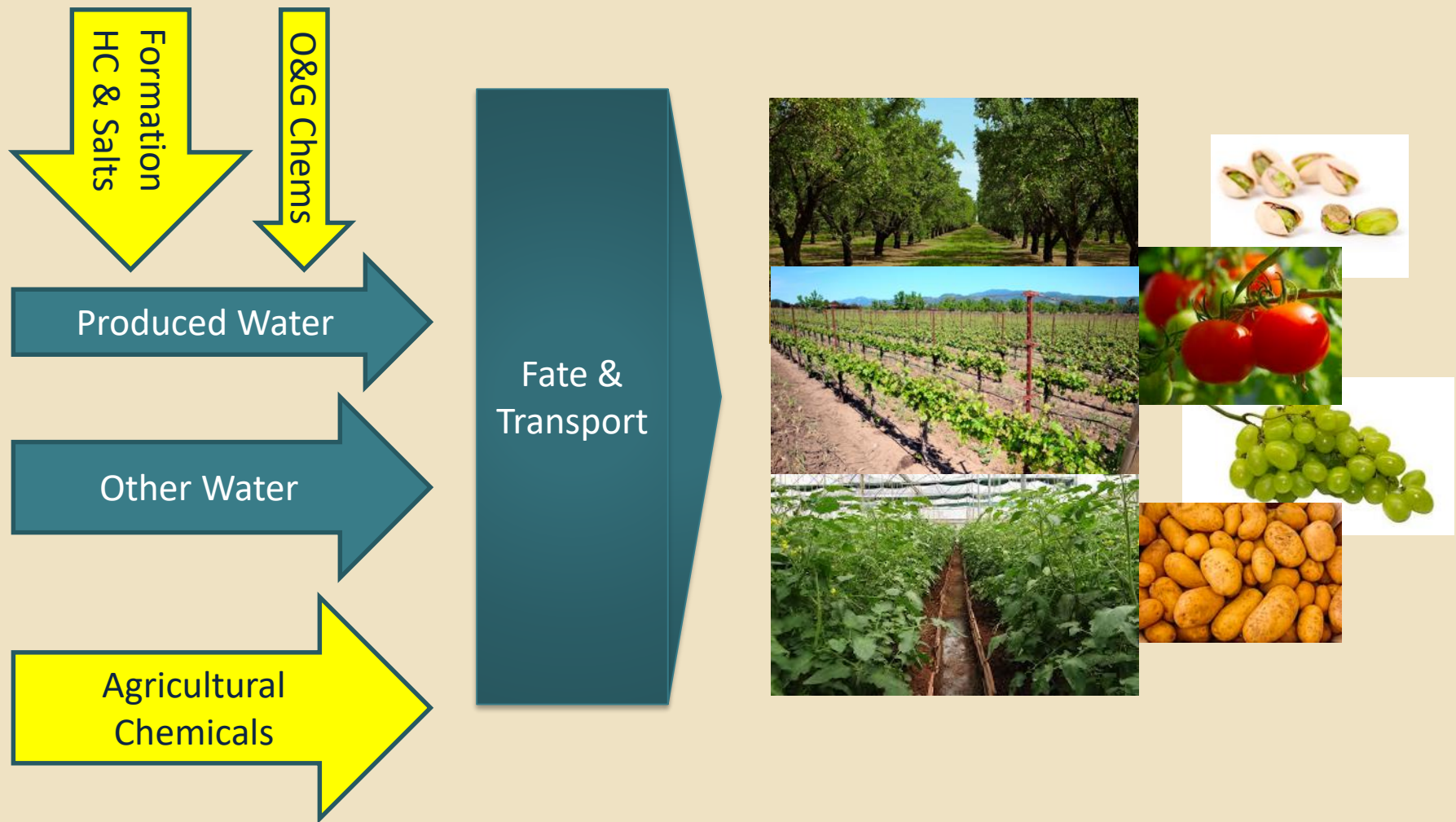
- 1. Selection of “Chemicals of Interest”, from a list of known chemical additives and naturally occurring chemicals in produced water, for further evaluation**
- 2. Literature review focusing on the “Chemicals of Interest” in the context of produced water reuse in agriculture irrigation and other potential sources of these chemicals in the agricultural water supply**
- 3. Sampling and chemical analysis of crops irrigated with produced water in the Central Valley**

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# TASK 1: PRODUCED WATER - FROM FIELD TO FIELD



# TASK 1: IDENTIFY THE CHEMICALS OF INTEREST

## What is in produced water?

- **Additives**
  - To date, lists provided from the producers to the Water Board included 377 entries
  - Many entries are duplicates
  - Total # of unique chemical additives: 306
  - Some overlap with naturally occurring compounds
- **Naturally occurring compounds identified from the literature**
  - 49 organic chemicals were identified
  - 46 inorganic constituents
    - 3 NORMS:  $\text{Ra}_{226}$ ,  $\text{Ra}_{228}$ , U

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**Total Chemicals to Evaluate = 385**

# TASK 1: CRITERIA IDENTIFIED IN SCOPE OF WORK TO EVALUATE THE LIST OF CHEMICALS

## How to evaluate the list of chemicals?

1. Oral toxicity information/data (with priority given to chronic mammalian toxicity data)
2. Dermal toxicity information/data
3. Carcinogenicity information/data
4. Teratogenicity information/data
5. Environmental persistence/degradation information/data including soil half-life
6. Degradation byproducts of the chemicals and their associated toxicities, carcinogenicity, teratogenicity, endocrine disrupting potential, etc.
7. Plant uptake information/data
8. Amounts and frequency of use in oil fields
9. Chemicals that are persistent, bioaccumulative, and toxic as defined by the US Environmental Protection Agency [EPA] and other government or scientific organizations
10. Chemicals detected in any water quality analyses of irrigation water with maximum measured irrigation water concentrations above available risk-based water screening levels (for example, EPA drinking water screening levels or California Public Health Goals)
11. Ambient, background concentrations in air and water that can result from agricultural practices and human activities unrelated to produced water reuse
12. Whether the chemical is naturally occurring in the environment
13. Other sources of the chemical in the environment and the specificity of the chemical to application of produced water for irrigation



# TASK 1: EVALUATING THE LIST OF CHEMICALS

## How to evaluate the list of chemicals?

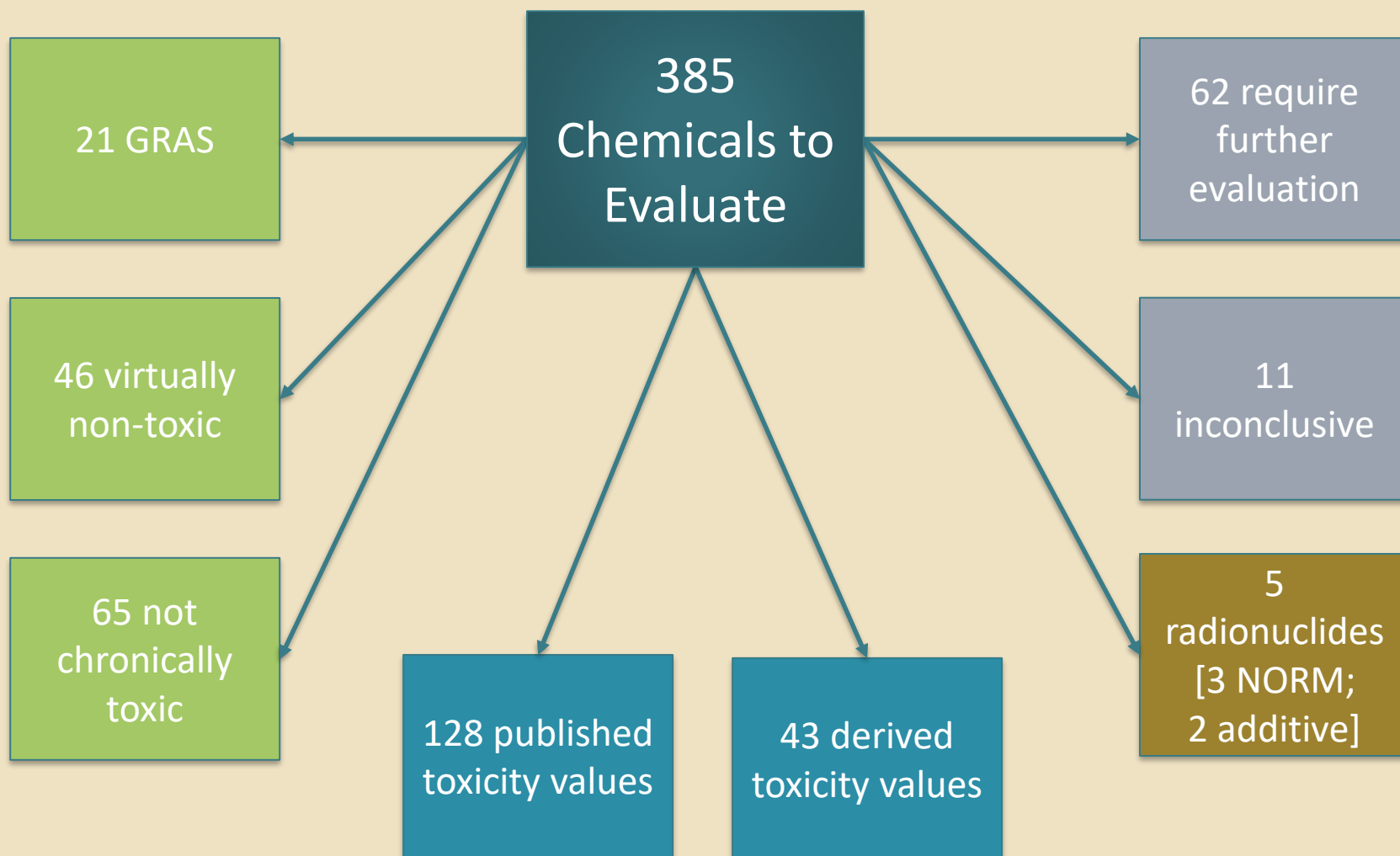
1. **Oral toxicity information/data (with priority given to chronic mammalian toxicity data)**
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# TASK 1: PRIMARY EVALUATION BASED ON TOXICITY

1. Identify published chronic toxicity values for the chemicals on the list
2. From chemicals without toxicity values, use the Food and Drug Administration (FDA) list of chemicals that are Generally Recognized as Safe (GRAS) to identify a sub-list of chemicals that are unlikely to be of concern, given the low level of these chemicals likely to be present in produced water. If published toxicity values were available, which was the case for some of the inorganic compounds, the compound would remain in the list identified in (1).
3. From the remaining chemicals—after (1) and (2)—research the available peer reviewed literature, government/industry reports, and relevant databases to identify data that characterizes the toxic potential of the remaining chemicals as it relates to chronic oral exposures.
4. Identify the sub-list of chemicals that do not have any data that characterizes their toxic potential related to chronic oral exposures.
5. From the remaining chemicals—after (1), (2), (3), and (4)—create three sub-lists that represent: chemicals with unknown chronic toxicity, chemicals with no apparent chronic toxicity, and chemicals with apparent chronic toxicity.
6. For those chemicals without published toxicity values where the available scientific literature suggests toxicity related to chronic oral exposure, GSI developed toxicity values based on the scientific literature.



# TASK 1: SUMMARY OF TOXICITY EVALUATION



# TASK 1: PUBLISHED TOXICITY VALUES

- United States Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS) Reference Dose (RfD)
- EPA IRIS Oral Slope Factor for Cancer
- EPA Provisional Peer-Reviewed Toxicity Values (PPRTV) Oral RfD
- PPRTV Oral Slope Factor
- Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Level (MRL) Oral Chronic Exposure
- Office of Environmental Health Hazard Assessment (OEHHA) Oral Slope Factor
- OEHHA Child Specific RfD
- OEHHA Cancer No Significant Risk Level (NSRL) Oral Exposure
- OEHHA Reproductive/Developmental Maximum Allowable Daily Dose (MADL) Oral Exposure
- USGS Noncancer Human Based Screening Levels (HBSL)
- USGS Cancer HBSL
- Human Health Toxicity Values in Superfund Risk Assessments (HEAST) Oral Slope Factor
- HEAST Chronic Oral Reference Dose
- HEAST Oral Exposure NOAEL
- Other Toxicity Values Derived to Protect Health

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**Chemicals with Published Toxicity Values = 128**

# TASK 1: GRAS AND VIRTUALLY NON-TOXIC CHEMICALS

- **Generally Regarded As Safe (GRAS)**
  - An FDA designation that a substance added to food is considered safe by experts
- **Virtually non-toxic in the concentrations likely to be present in produced water**
  - Food additives
  - Health Supplements
  - Are known to be virtually non-toxic
  - Inert
  - Hydrolyze with inert breakdown products



**21 GRAS  
+ 46 Virtually Non-Toxic**

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**66 Non-toxic chemicals\***

\*at concentrations likely to be observed in produced water

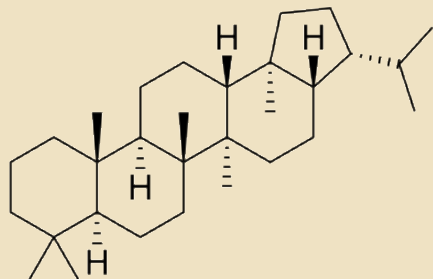
# TASK 1: OTHER CHEMICALS WITHOUT CHRONIC TOXICITY

- Based on a review of the scientific/toxicological literature
  - In repeated dose studies, NOEL—not NOAEL—were in the range of 100's to 1000's mg/kg/d
  - Effects observed were not toxicologically relevant
    - Lesions in the forestomach (no structure in humans)
    - $\alpha$ -2u-globulin nephropathy and related cancer is specific to the male rat



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**Chemicals without evidence of chronic toxicity at levels expected in produced water = 65**



# TASK 1: CHEMICAL WITH INCONCLUSIVE TOXICITY

- **Possibly suggestive, but insufficient studies to make a determination**
  - Acrolein Dimer shows some indications of chronic toxicity, albeit lower than its monomer, but data is not sufficient to derive a RfD
- **Ambiguous chemical definition**
  - Aromatic Amines (No CASRN: some are carcinogenic)
  - Sorbitan Ester (No CASRN: sorbitan monostearate, sorbitan tristearate, and sorbitan monolaurate, other?)
- **Conflicting, or incomplete, scientific data**
  - Quinladine has low oral toxicity but some suggestion of mutagenicity in bacterial assays, but the assay results are inconsistent

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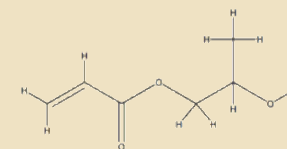
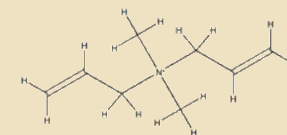
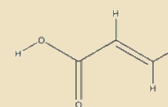
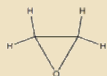
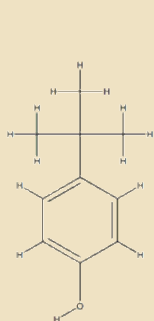
**Chemicals with inconclusive toxicity = 11**

# TASK 1: CHEMICALS THAT REQUIRE FURTHER EVALUATION

- A number of chemicals couldn't be assessed for chronic oral toxicity
  - No toxicologic data available
  - No evident read-across chemicals
  - Only assessed for acute exposure studies, missing oral studies, and route-to-route extrapolation not possible
  - Surfactants and polymers

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Chemicals requiring further evaluation = 62





# **TASK 1: DERIVING TOXICITY VALUES FOR CHEMICALS WITHOUT AGENCY VALUES**

- **Based on the available animal data, GSI derived toxicity values**
- **Only non-cancer outcomes were assessed**
- **There were no toxicologically relevant cancer outcomes found during the review of the animal studies**

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**Chemicals with derived toxicity values = 43**

# TASK 1: DERIVING TOXICITY VALUES FOR CHEMICALS WITHOUT AGENCY VALUES

- For chemicals with supporting animal data, GSI developed toxicity values similar to a Reference Dose (RfD)
- This is the approach employed by many agencies to derive toxicity reference values (e.g., US EPA, ATSDR, OEHHA)



# TASK 1: DERIVING TOXICITY VALUES FOR CHEMICALS WITHOUT AGENCY VALUES

1. A suitable no observed adverse effect level (NOAEL) is identified
  - Toxicologically relevant
  - Lowest dose observed, if multiple studies
  - When not available a lowest observed adverse effect levels (LOAEL) is used
2. Uncertainty factors,  $U_i$ , are applied to the NOAEL-LOAEL depending on the applicable study's parameters

$$RfD = \frac{NOAEL \text{ or } LOAEL}{\prod U_i}$$

	Animal to Human Size Scaling	Other Animal to Human Differences	Susceptible Populations	Sub-chronic to Chronic	LOAEL to NOAEL	Study Quality
RANGE	1.1 - 12.3	1 - 10	10	1, 10	1, 10	1 - 10

# TASK 1: DERIVING TOXICITY VALUES FOR CHEMICALS WITHOUT AGENCY VALUES

CASRN	Chemical Name	Notes	Toxicity Value (mg/kg/d)
79-06-1	Acrylamide	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000002
53-70-3	Dibenzo(a,h)anthracene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.0000024
50-32-8	Benzo(a)pyrene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000003
119-65-3	Isoquinoline	1 in 100000 cancer risk dose (US EPA, IRIS); read-across with quinoline	0.000003
111-44-4	Bis (2-chloroethyl) ether	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000004
205-99-2	Benzo(b)fluoranthene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000008
193-39-5	Indenopyrene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000008
56-55-3	Benzo(a)anthracene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.000008
100-44-7	Benzyl chloride	1 in 100000 cancer risk dose (US EPA, IRIS)	0.00006
218-01-9	Chrysene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.00008
91-20-3	Naphthalene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.00008
123-91-1	1,4 Dioxane	1 in 100000 cancer risk dose (US EPA, IRIS)	0.0001
71-43-2	Benzene	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.0001
7440-43-9	Cadmium	MRL (ATSDR)	0.0001
7439-97-6	Mercury	REL (OEHHA)	0.00016
7440-48-4	Cobalt	RfD (US EPA, PPRTV)	0.0003
7440-36-0	Antimony	RfD (US EPA, IRIS)	0.0004
7440-38-2	Arsenic	RfD (US EPA, IRIS)	0.0004
50-00-0	Formaldehyde	1 in 100000 cancer risk dose (CalEPA, OEHHA)	0.00048
107-02-8	Acrolein	RfD (US EPA, IRIS)	0.0005

# TASK 1: DEVELOPING SCREENING LEVELS BASED ON TOXICITY VALUES

**One day consumption rates at the 90<sup>th</sup> percentile**

Commodity	90th Percentile Consumption [kg/d]	90th Percentile Consumption [kg/bw-d]
Citrus	0.192	0.00451
Garlic	0.0017	0.00003
Grapes	0.151	0.00365
Carrots	0.073	0.00091
Almonds	0.0194	0.0004
Pistachios	0.096	0.001
Potatoes	0.239	0.0034

# TASK 1: DEVELOPING SCREENING LEVELS BASED ON TOXICITY VALUES

## Produce-Specific Screening Concentration [mg/kg<sub>produce</sub>]

Chemical	Toxicity Value [mg/kg-d]	Citrus	Garlic	Almonds	Pistachios
Acrolein	0.0005	0.11	17	1.3	0.5
Molybdenum	0.005	1.11	167	13	5
Copper	0.01	2.22	333	25	10
Nickel	0.011	2.44	367	28	11
Barium	0.2	44	6667	500	200
Zinc	0.3	67	10000	750	300
Strontium	0.6	133	20000	1500	600
Acetone	0.9	200	30000	2250	900
Methanol	2	443	66667	5000	2000



# TASK 1: DEVELOPING SCREENING LEVELS BASED ON TOXICITY VALUES

**Max. Measured Conc. in Treated Produce [mg/kg<sub>produce</sub>]**

Chemical	Toxicity Value [mg/kg-d]	Citrus	Garlic	Almonds	Pistachios
Acrolein	0.0005	--	3.1	--	--
Molybdenum	0.005	--	0.61	0.56	--
Copper	0.01	0.85	2.5	9.7	5.5
Nickel	0.011	--	--	1.3	--
Barium	0.2	0.91	1.9	2.1	1
Zinc	0.3	--	11	32	12
Strontium	0.6	3.2	2.5	9.5	3.7
Acetone	0.9	0.75	0.4	--	2.1
Methanol	2	380	--	--	--

# TASK 1: DEVELOPING SCREENING LEVELS BASED ON TOXICITY VALUES

$$\text{Hazard Quotient} = \frac{\text{Max Conc.}}{\text{Screening Conc.}}$$

Chemical	Toxicity Value [mg/kg-d]	Citrus	Garlic	Almonds	Pistachios
Acrolein	0.0005	--	0.19	--	--
Molybdenum	0.005	--	0.004	0.045	--
Copper	0.01	0.45	0.008	0.39	0.6
Nickel	0.011	--	--	0.047	--
Barium	0.2	0.02	0.0003	0.0042	0.005
Zinc	0.3	--	0.0011	0.043	0.04
Strontium	0.6	0.024	0.00013	0.006	0.006
Acetone	0.9	0.004	0.000013	--	0.002
Methanol	2	0.86	--	--	--

# TASK 1: FATE AND TRANSPORT

- **GSI has compiled biodegradability-in-water data of most of the chemicals**
  - Based on waste water testing
  - Bacterial inoculum is added to the sample
  - It is uncertain how results from these “enriched” conditions translate to produced water in an irrigation setting
- **Similar issues arise with assessing biodegradability in soil**
  - Uncertainty is compounded by quick uptake of water by plants during rapid growth, especially during fruit development
  - How does sorption properties of chemicals affect biodegradability and mobility in soil

# TASK 1: FATE AND TRANSPORT

- **Ongoing work**
  - translate OECD biodegradation data to irrigation setting
  - fugacity of chemicals in water
  - sorption potential of chemicals
  - other mechanisms of physical degradation (hydrolysis, photolysis)
- **Uncertainties raise the question about how useful comprehensive quantitative fate and transport analysis for all chemicals will be**
  - Focused assessment on selected chemicals (most toxic)

# TASK 2: HOW TO DO WE GET TO, AND WHERE ARE WE GOING FROM HERE?

- **Focusing on most toxic:**
  - **Continue paring down the list of chemical based on fate and transport parameters**
    - We need more details on the timeline and processes related to produced water from oil field to crops here
    - Will require a chemical by chemical assessment
- **Task 2: The Literature Review**
  - **Produced water in agriculture**
  - **Other sources of the chemicals, ambient levels, and levels in food**
  - **In depth discussion of chemicals' toxicity**
  - **Specific fate and transport issues related to list of chemicals**
  - **Available literature on plant uptake for the list of chemicals**
  - **Address “Chemicals requiring further evaluation”**



**Thank you**

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